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Scattering of Electrons from H_2^+: The Method of Polarized Single-Center Orbitals

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A generalization of the method of polarized orbitals is introduced to calculate the scattering of electrons from diatomic molecules in the Born–Oppenheimer (fixed-nuclei) approximation. The molecule is described by a single-center expansion which in lowest order is spherically symmetric and therefore an atomic-like function. This function can be polarized in complete analogy with an atomic orbital. Furthermore, the first approximation beyond the spherically symmetric can be included to give a permanent distortion correction. In the s-wave results, the induced polarization effects are larger than the first-order correction. The p-wave phase shifts are in some cases much larger than the s wave, and very complicated by virtue of the combined effects of exchange, polarization, and first permanent distortion. The method also yields, as a by-product of the polarizability of H_2^+. The first part of the paper contains a general analysis of the partial-wave expansion from diatomic molecules in the Born–Oppenheimer approximation. The scattered amplitude is given in terms of phase shifts which are independent of the angles between the internuclear axis and the incident direction. The dependence on these angles is shown to be factorable and analytically expressible independent of the dynamical problem.

I. INTRODUCTION

FOR atoms (or atomic ions) whose polarizabilities are not too large, one may fairly say that the chief theoretical ideas are in hand which are necessary for the calculation of low-energy scattering of electrons from them. These ideas can be described as the consistent incorporation of exchange and polarization. In the case of electron scattering from diatomic molecules (or molecular ions) one has, in addition to the above effects, the further complications which arise from a two-centered target and its additional degrees of freedom. The simplest approximation to make with regard to these additional degrees of freedom is that they are frozen out. This is what we shall do throughout this paper, so that we assume the nuclei are fixed in space, neither rotating nor vibrating; and this is what we shall mean by the Born-Oppenheimer approximation.

Although the introduction of such an approximation at the very outset does not allow one to see how it develops from a theory in which the nuclear motion is included, it is quite clear that for all but the smallest energies such a fixed-nucleus approximation must be realistic. Specifically, for electron velocities large compared to the rotational and vibrational velocities of the nuclei, all of the interaction takes place while the nuclei are essentially fixed in space. In terms of energy this condition reduces to

$$k^2 \gg (m/M)\, E_{r,v},$$

where k^2 and m are the (impacting) energy and mass of the electron, and M, $E_{r,v}$ the mass and (nonelectronic) energy of the molecule. For most diatomic molecules this means that the fixed-nucleus approximation should be valid in some meaningful sense for impacting energies above as little as 10^{-3} eV.

The natural approach to the fixed-nucleus approximation is the use of a two-centered coordinate system,[1] i.e. an ellipsoidal coordinate system, in which the two foci correspond to the equilibrium positions of the nuclei. However, unless the effective potential in which the scattered electron moves is separable in these coordinates, the technical difficulties of working with such coordinates more than offsets any apparent geometrical advantages they may appear to contain.[2] Yet it is clearly naive to expect that the effective potential seen by the scattered electron will be separable in these or any coordinates if accurate account is taken of the interaction with the orbital electrons.

In addition to the disadvantages of an ellipsoidal system one can invoke good physical arguments in favor of a spherical coordinate description, if one assumes that the internuclear separation is not too large. For in that case the paths of the orbital electrons will tend to encircle both nuclei and thereby present the incoming electron with a charge cloud, somewhat distorted to be sure, but not too much unlike, qualitatively speaking, the kind of cloud it would see if the target were an atom. Particularly if the energy of the incoming electron is small can we be sure that its long wavelength will not allow it to probe the detailed structure of the molecular core.

The chief idea of the method we shall present here is the utilization of such a spherical coordinate system

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[1] J. F. Fisk, Phys. Rev. **49**, 167 (1936); H. Stier, Z. Physik **76**, 439 (1932).

[2] H. S. W. Massey and R. O. Ridley, Proc. Phys. Soc. (London) **A69**, 659 (1956).

to describe both the target molecule and the scattered electron so that we may exploit to the maximum extent all the analogies of the resultant description with electron-atom scattering. This includes both exchange and polarization. In addition we can include, at least for the case at hand, the main specifically molecular permanent distortion effect of the axially symmetric molecule and treat it in close analogy with the induced polarization effects. For this reason we shall call our approach "the method of polarized single-center orbitals."

The application which we shall consider is electron scattering from H_2^+. This experimentally somewhat inaccessable target is obviously motivated by its simplicity, being the only one-electron homonuclear diatomic molecule (aside from isotopic variations) that there is. At the price of not being able simply to compare with experiment, we have the advantages of a two-electron problem with the rather simple and well calculated single-center expansion of the one-electron target molecular ion available.[3]

As stated above, the method that we shall project assumes that the nuclei are fixed during the whole scattering process (Born–Oppenheimer approximation). Within this idealization we further make a partial-wave analysis. This causes some complications on two accounts. First because total angular momentum is not conserved in the Born–Oppenheimer approximation, there is coupling among different partial waves. Second there is a parametric dependence of the scattering on the angles describing the orientation of the internuclei axis with respect to the incoming direction. This is a general problem[4] in which, in our opinion, the previous literature has been misleading in that it gives the impression that the only correct way to solve this problem is for the phase shifts to depend parametrically on those angles. However, we shall show that one can *consistently* set up the dynamical problem to be independent of those angles, so that they enter the scattered amplitude as geometrical factors which may be computed independently of the phase shifts. All these matters will be the subject Sec. II.

In Sec. III we deal with the actual method of polarized single-center orbitals and its application to $e-H_2^+$ scattering, deriving the radial equations for s and p partial waves. Section IV presents results in an ascending sequence of approximations which we are naturally led to consider. The section concludes with a discussion of further generalizations and applications of the method.

II. PARTIAL-WAVE DECOMPOSITION OF THE SCATTERED WAVE IN THE BORN-OPPENHEIMER APPROXIMATION

Let the direction of the incident electron beam define the z axis of a laboratory-fixed coordinate system, and let the internuclear axis of the diatomic molecule describe the z axis of a body-fixed coordinate system. In the following we shall always use primes for coordinates in the laboratory-fixed coordinate system and unprimed coordinates for the body-fixed system. Let us further remind the reader that whereas it requires only two (spherical) angles to define the direction of a vector in space with respect to a given coordinate system, three (Euler) angles are needed to define one coordinate system rotated with respect to another.

Now let us write the most general expansion of a wave function of the scattering electron. Such a function will depend both on its coordinates $\mathbf{r}$ in the body-fixed frame and on the orientation of that frame with respect to the laboratory frame. Thus we can write

$$\psi(\mathbf{r})=r^{-1}\sum_{i,j,j'}u_{l_im_i,l_jm_jm_j'}(r)\times Y_{l_im_i}(\Omega)\mathfrak{D}_{m_jm_j'}{}^{(l_j)*}(\alpha_0,\beta_0,\gamma_0). \qquad (2.1)$$

This expansion is general because the Y_{lm} and the $\mathfrak{D}_{mm'}{}^{(l)}$, the latter being the rotational harmonics,[5] are complete sets in their respective spaces. We have written ψ as a function of $\mathbf{r}$ rather than $\mathbf{r}'$, because the Hamiltonian, in the Born–Oppenheimer approximation, is a single (operator) function of $\mathbf{r}$, which is *independent* of the Euler angles α_0, β_0, γ_0. Thus any reasonable equations that one will derive for the functions $u_{i,jj'}(r)$ $[\equiv u_{l_im_i,l_jm_j'}(r)]$ will be independent of the j, j' indices. In particular the asymptotic forms of the functions will give rise to phase shifts which are independent of j, j' indices:

$$\lim_{r\to\infty} u_{i,jj'}(r)=k^{-1}A_{m_im_jm_j'}{}^{(l_il_j)}\sin(kr-\tfrac{1}{2}(\pi l_i)+\eta_{l_im_i}). \qquad (2.2)$$

(In the above we assume that we are dealing with non-Coulomb forces so that the $\eta_{l_im_i}$ are ordinary phase shifts.[6]) On the other hand, the amplitudes $A_{m_im_jm_j'}{}^{(l_il_j)}$ can depend on j, j'; in fact the $A_{m_im_jm_j'}{}^{(l_il_j)}$ are determined by the condition $\exp(i\mathbf{k}\cdot\mathbf{r}')-\psi(\mathbf{r})$ contain only outgoing radial waves in r'. To evaluate the above expression it is necessary to write the spherical angles of $\mathbf{r}$ in the laboratory coordinate system. The necessary

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[3] M. Cohen and C. A. Coulson, Proc. Cambridge Phil. Soc. **57**, 96 (1961); A. Temkin, J. Chem. Phys. **39**, 161 (1963). The coupling term in Eq. (2.4) contains a typographical error. Functions used in the present application were kindly computed by H. Rabinovitch [Cf., H. Rabinovich, J. Chem. Phys. **43**, 3144 (1965)].

[4] Cf., however, A. M. Arthurs and A. Dalgarno, Proc. Roy. Soc. (London) **A256**, 540 (1960). They have considered the scattering problem from the complementary point of view of the target being a rotator with angular momentum. This gives a natural approach to the problem of rotational excitation; however, within the framework of their method it is more difficult to include the specific interactions between the incoming and orbital electrons.

[5] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957). The $\mathfrak{D}$ functions unfortunately have no universally accepted name; we here propose the name "rotational harmonics" for them. Aside from normalization they are identical to the $\mathfrak{D}$ functions used in A. K. Bhatia and A. Temkin, Rev. Mod. Phys. **36**, 1050 (1964). The phase of these functions is given in an explicit form there.

[6] We here concede, particularly to our British colleagues, in calling phase shifts η rather than δ. This concession has been necessitated by the double subscript notation in order to avoid confusion with the Kronecker delta which is also used throughout this paper.

transformation is given by[5]

$$Y_{l_i m_i}(\Omega)=\sum_{m_i'} Y_{l_i m_i'}(\Omega')\mathfrak{D}_{m_i' m_i}{}^{(l_i)}(\alpha_0,\beta_0,\gamma_0). \quad (2.3a)$$

Substituting (2.3a) into the asymptotic form of (2.1) and collecting the coefficient of the ingoing radial waves, we find the condition that must be satisfied in order that this coefficient be zero is ($\mathfrak{B}_0\equiv\alpha_0,\beta_0,\gamma_0$):

$$\sum_{m_i,m_j,m_j'} \exp(-i\eta_{l_i m_i})A_{m_i m_j m_j'}{}^{(l_i l_j)}\mathfrak{D}_{m_i' m_i}{}^{(l_i)}(\mathfrak{B}_0)$$

$$\times\mathfrak{D}_{m_j m_j'}{}^{(l_j)*}(\mathfrak{B}_0)=i^{l_i}[4\pi(2l_i+1)]^{1/2}\delta_{l_i l_j}\delta_{m_i' 0}. \quad (2.3b)$$

A sufficient condition for this to hold is

$$A_{m_i m_j m_j'}{}^{(l_i l_j)}=i^{l_j}[4\pi(2l_i+1)]^{1/2}$$

$$\times\exp(i\eta_{l_i m_i})\delta_{m_i m_j'}\delta_{m_j 0}\delta_{l_i l_j}. \quad (2.4)$$

The verification of this relies on the relationship[5]

$$\sum_{m_i}\mathfrak{D}_{m_i' m_i}{}^{(l)}(\mathfrak{B}_0)\mathfrak{D}_{0 m_i}{}^{(l)*}(\mathfrak{B}_0)=\delta_{0 m_i'}. \quad (2.5)$$

We can thus characterize the amplitudes $A_{m_i m_j m_j'}{}^{(l_i l_j)}$ by a single superscript $l\equiv l_i=l_j$. With this simplification the outgoing wave has the form

$$\lim_{r\to\infty}[\psi-\exp(i\mathbf{k}\cdot\mathbf{r}')]$$

$$=[\exp(ikr)/r]\{[1/2ik]\sum_{l,m_i'}[4\pi(2l+1)]^{1/2}[\sum_{m_i}\exp(2i\eta_{lm_i})$$

$$\times\mathfrak{D}_{m_i' m_i}{}^{(l)}(\mathfrak{B}_0)\mathfrak{D}_{0 m_i}{}^{(l)*}(\mathfrak{B}_0)-\delta_{m_i' 0}]Y_{lm_i'}(\Omega')\} \quad (2.6a)$$

$$\equiv[\exp(ikr)/r]\sum_{l,m_i'}f_{lm_i'}(\mathfrak{B}_0)Y_{lm_i'}(\Omega'), \quad (2.6b)$$

where $f_{l,m_i'}(\mathfrak{B}_0)$ is, aside from $Y_{lm_i'}$, the quantity in curly brackets in (2.6a). This expression can be rewritten in a more familiar form if we use the expression (2.5) for the Kronecker delta:

$$f_{lm_i'}(\mathfrak{B}_0)=\{[4\pi(2l+1)]^{1/2}/k\}\sum_{m_i}\exp(i\eta_{lm_i})$$

$$\times\sin\eta_{lm_i}\mathfrak{D}_{m_i' m_i}{}^{(l)}(\mathfrak{B}_0)\mathfrak{D}_{0 m_i}{}^{(l)*}(\mathfrak{B}_0). \quad (2.7)$$

Equation (2.7) is the desired relation for the scattered amplitude. It expresses the amplitude in terms of orientation-independent (but *m*-dependent) phase shifts η_{lm}, the explicit dependence on the orientation of the internuclear axis being carried in the product of the $\mathfrak{D}$ functions.

For practical purposes it is necessary to square $f_{lm_i'}$ and average over directions of the internuclear axis; this gives the differential scattering into a laboratory angle Ω'; define this quantity to be $\bar{\sigma}(\Omega')$:

$$\bar{\sigma}(\Omega')\equiv(8\pi^2)^{-1}\int|\sum_{l,m_i'}f_{lm_i'}(\beta_0)Y_{lm_i'}(\Omega')|^2 d\alpha_0 d\gamma_0\sin\beta_0 d\beta_0. \quad (2.8a)$$

One finds after some Racah-algebra manipulation from (2.6b) and (2.7):

$$\bar{\sigma}(\Omega')=(1/k^2)\sum\frac{(2l+1)(2\lambda+1)}{(2L+1)}(l\lambda 00\mid L0)^2$$

$$\times(l\lambda m\mu\mid Lm+\mu)^2\cos(\eta_{lm}-\eta_{\lambda\mu})\sin\eta_{lm}\sin\eta_{\lambda\mu}P_L(\cos\theta'), \quad (2.8b)$$

where the $(l\lambda m\mu\mid LM)$ are Clebsch-Gordan coefficients[7] and the sum goes over all indices. In practice the sum will be finite and will be determined by the number of partial waves ($l_{\max}=\lambda_{\max}$) that one will include in a calculation. The index L will assume all values consistent with vector coupling and parity, the latter implying by virtue of the $(l\lambda 00\mid L0)$ coefficient that

$$l+\lambda+L=\text{even integer}. \quad (2.9)$$

Some simplification in (2.8b) will also ensue from the relation

$$\eta_{lm}=\eta_{l,-m}, \quad (2.10)$$

which holds for scattering from a homonuclear diatomic molecule.

Finally, the total integrated cross section integrated over Ω' reduces to

$$Q\equiv\int\bar{\sigma}(\Omega')d\Omega'=(4\pi/k^2)\sum_{l,m}\sin^2\eta_{lm}. \quad (2.11)$$

All the above formulas can easily be shown to reduce to the well-known results of ordinary atomic scattering theory when the phase shifts η_{lm} become independent on m.

In the application we shall be concerned with here, the target ($H_2{}^+$) has a net charge, so that the total cross section is infinite and the angular distribution contains a contribution from the pure Coulomb field and a cross term. The modification is well known[8] and the angular distribution formula for $e-H_2{}^+$ is scattering is

$$\bar{\sigma}_c(\Omega')=[4k^2\sin^4(\tfrac{1}{2}\theta')]^{-1}+[k^3\sin^2(\tfrac{1}{2}\theta')]^{-1}\sum_{l,m\geq 0}\sin\eta_{lm}$$

$$\times\cos[(1/k)\ln(\sin^2(\tfrac{1}{2}\theta'))+2(\sigma_0-\sigma_l)-\eta_{lm}]$$

$$\times(2-\delta_{m0})P_l(\cos\theta')+\hat{\sigma}(\Omega'), \quad (2.12)$$

where $\hat{\sigma}(\Omega')$ is the same as $\bar{\sigma}(\Omega')$ of Eq. (2.8b) except that the argument of the cosine function becomes $(\bar{\eta}_{lm}-\bar{\eta}_{\lambda\mu})$, where

$$\bar{\eta}_{lm}=2\sigma_l+\eta_{lm} \quad (2.13)$$

and

$$\sigma_l=\arg[\Gamma(l+1-ik^{-1})]. \quad (2.14)$$

III. THE METHOD OF POLARIZED SINGLE-CENTER ORBITALS: APPLICATION TO $e-H_2{}^+$ SCATTERING

Up to this point we have not as yet presented a method for actually calculating scattering, that is,

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[7] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1935).

[8] L. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949).

TABLE I. Radial functions[a] involving H_2^+ ($R_{AB}=2$).

	$\varphi^{(\mathrm{pol})}(r)$	$\varphi_0^{(0)}(r)$	$\varphi_0^{(2)}(r)$	$\varphi_2^{(2)}(r)$
r	$E_0=-1.037$ Ry		$E_2=-1.167$ Ry	
0.2	6.28×10^{-2}	2.21×10^{-1}	2.20×10^{-1}	2.57×10^{-3}
0.4	2.62×10^{-1}	4.25	4.24	1.91×10^{-2}
0.6	5.52	5.96	5.97	5.69
0.8	8.92	7.20	7.25	1.10×10^{-1}
1.0	1.23×10^{0}	7.88	7.94	1.57
1.2	1.51	7.98	8.01	1.71
1.4	1.72	7.67	7.625	1.63
1.6	1.86	7.10	6.98	1.47
1.8	1.93	6.40	6.215	1.27
2.0	1.94	5.65	5.42	1.08
2.2	1.91	4.90	4.64	8.98×10^{-2}
2.4	1.83	4.20	3.93	7.40
2.6	1.73	3.55	3.29	6.035
2.8	1.61	2.98	2.72	4.89
3.0	1.48	2.48	2.24	3.93
3.2	1.34	2.05	1.83	3.15
3.4	1.21	1.69	1.485	2.51
3.6	1.07	1.38	1.20	2.00
3.8	9.49×10^{-1}	1.12	9.65×10^{-2}	1.58
4.0	8.32	9.07×10^{-2}	7.73	1.25
4.5	5.81	5.27	4.37	6.82×10^{-3}
5.0	3.93	3.01	2.42	3.69
5.5	2.58	1.69	1.33	1.97
6.0	1.66	9.39×10^{-3}	7.17×10^{-3}	1.04
6.5	1.04	5.16	3.84	5.49×10^{-4}
7.0	6.44×10^{-2}	2.81	2.04	2.87
7.5	3.92	1.52	1.07	1.49
8.0	2.36	8.16×10^{-4}	5.62×10^{-4}	7.71×10^{-5}
9.0	8.24×10^{-3}	2.32	1.52×10^{-4}	2.04
10.0	2.77	6.455×10^{-5}	4.025×10^{-5}	4.64×10^{-6}
15.0	8.24×10^{-6}	9.13×10^{-8}	4.46×10^{-8}	5.57×10^{-9}
20.0	1.69×10^{-8}	1.09×10^{-10}	4.20×10^{-11}	5.10×10^{-12}
30.0	4.13×10^{-14}	1.22×10^{-16}	2.95×10^{-17}	3.01×10^{-18}

[a] Any entry not explicitly multiplied by a power of 10 is understood to be multiplied by the same power of 10 as the last explicitly given one above it.

specifically for calculating the phase shifts η_{lm}. The development of the previous section does imply that the scattered electron will ultimately be described in a spherical coordinate system, but clearly there is no unique way of doing this. The essential idea that we present for deriving such equations is the use of a single-center expansion of the target molecule. In the case of H_2^+ the target wave function with spherical coordinates r_2, Ω_2 centered the midpoint of its internuclear axis (z-axis) can be expanded in the form[3]

$$\Phi_M^{(N)}(\mathbf{r}_2)=\sum_{n=0}^{N}{}'' \frac{\varphi_n^{(N)}(r_2)}{r_2}Y_{nM}(\Omega_2). \qquad (3.1)$$

The double prime in (3.1) signifies every second value of summation index, and $M=0$, 1, 2, $\cdots$ corresponds to Σ, Π, Δ, $\cdots$ states (for further details, cf. Ref. 3). In principle the n summation is infinite, but in practice it must be truncated at some point $n=N$ which defines the order of approximation to which one is treating the target. At $N=0$ (zeroth order) it can be seen that the wave function is an eigenfunction of the total angular momentum of the target electron, and thus it is in complete analogy with an atomic orbital. It is the central point of the present method to suggest that this approximation is a suitable starting point for calculating scattering. In particular corrections to this approximation will be treated as small in the sense that quadratic terms involving such corrections will never be included. In the sequel we shall be concerned only with the ground (Σ_g) state of the target ($M=0$).

What are these corrections? Clearly the induced polarization of the orbital electron by the incoming one is a major perturbation. The solution of this problem that was proposed in the method of polarized orbitals[9] was the use of Sternheimer's method[10] to calculate a polarized increment to the orbital. This in turn is based on the adiabatic approximation in terms of which such distortion is calculated in an approximate form of perturbation theory corresponding to the incident electron being fixed at an arbitrary point $\mathbf{r}_1$. In the zeroth-order approximation for the target electron, the equation for the polarized orbital can readily be derived in analogy with the polarization of H.[11]

$$\left[\frac{d^2}{dr^2}-\frac{2}{r^2}+V_0(r)-\frac{2}{R_{AB}}+E_0\right]\varphi_0^{(\mathrm{pol})}(r)=-2r\varphi_0^{(0)}(r). \qquad (3.2)$$

E_0-2/R_{AB} is the electronic part of the H_2^+ energy in

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[9] A. Temkin, Phys. Rev. **107**, 1004 (1957).

[10] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).

[11] A. Temkin, Phys. Rev. **116**, 358 (1959).

its ground (Σ_g) state in zeroth order and

$$V_l(r)=4g_l(r,\tfrac{1}{2}R_{AB}), \qquad (3.3a)$$

$$g_l(x,y)=x^l/y^{l+1}, \quad x<y$$
$$=y^l/x^{l+1}, \quad x>y. \qquad (3.3b)$$

The solution of this equation together with other important radial functions is given in Table I. As a byproduct one obtains the (dipole) polarizability of the H$_2^+$ ion:

$$\alpha_d=\tfrac{2}{3}\int_0^\infty \varphi_0^{(0)}(r)\,r\varphi_0^{(\mathrm{pol})}(r)\,dr. \qquad (3.4)$$

Numerically this turns out to be

$$\alpha_d=3.078a_0^3,$$

where we have displayed the units a_0^3 (Bohr radii-cubed) explicitly. This is to be compared to the mean (of perpendicular and parallel) dipole polarizability $\alpha_d=(2.881\pm0.095)\ a_0^3$ deduced by Dalgarno and Lewis,[12] the errors bars representing the uncertainty in the value of the perpendicular polarizability.

The complete polarized part of the wave function is[11]

$$\Phi_0^{(\mathrm{pol})}(\mathbf{r}_1;\mathbf{r}_2)=\frac{-\epsilon(r_1,r_2)}{r_1^2}\,\frac{\varphi_0^{(\mathrm{pol})}(r_2)}{r_2}\,\frac{P_1(\cos\theta_{12})}{(4\pi)^{1/2}}. \qquad (3.5)$$

The step function $\epsilon(r_1,r_2)$ provides not only a natural cutoff to the polarized part of the wave function but, understood as the limit of a smooth function which varies between 0 and 1 (as r_1 goes from being less than r_2 to being greater than r_2), it gives rise to well-defined terms in the radial equations we shall derive below.

The second major correction to the zeroth-order approximation comes from the fact that the molecular wave function is not an eigenfunction of total angular momentum, but rather is a superposition of angular momentum states corresponding to a permanent distortion of the charge cloud coming in turn from the two nuclei which define the target as a diatomic molecule. Here the very expansion (3.1) makes it clear what has to be done—we must go to higher order in N. In practice we shall go only to first order ($N=2$), our main concern being to test whether the first permanent distortion moment is in fact comparable to the induced polarizability in its effect on the phase shifts. The zeroth- and first-order wave functions of H$_2^+$ are also given[3] in Table I. The total wave functions which are to be used, then, are defined in two categories:

I. No polarization:

$$\Psi_{lm}^{(N)}=[u_{lm}(r_1)/r_1]Y_{lm}(\Omega_1)\Phi_0^{(N)}(\mathbf{r}_2)\pm(1\rightleftarrows2). \qquad (3.6a)$$

II. Polarization:

$$\Psi_{lm}^{(N)}=[u_{lm}(r_1)/r_1]Y_{lm}(\Omega_1)$$
$$\times[\Phi_0^{(N)}(\mathbf{r}_2)+\Phi_0^{(\mathrm{pol})}(\mathbf{r}_1;\mathbf{r}_2)]+(1\rightleftarrows2). \qquad (3.6b)$$

Within each category we have zeroth-order ($N=0$) and first-order ($N=2$) approximations. The ± sign in (3.6) refer to singlet (upper sign) and triplet (lower) state scattering.

With regard to the derivation of radial equations it has been our consistent philosophy to treat all corrections beyond the zeroth order as first-order corrections. Specifically this means that the radial equations are derived from[13]

$$\int\frac{\varphi_0^{(N)}(r_2)}{r_2}\,Y_{00}^*(\Omega_2)\,Y_{lm}^*(\Omega_1)[H-E_N]\Psi_{lm}^{(N)}d^3r_2d\Omega_1=0, \qquad (3.7a)$$

where (in units of rydbergs)

$$H=-\nabla_1^2-\nabla_2^2-\frac{2}{r_{A1}}-\frac{2}{r_{A2}}-\frac{2}{r_{B1}}-\frac{2}{r_{B2}}+\frac{2}{r_{12}}+\frac{2}{R_{AB}}. \qquad (3.7b)$$

As can be seen from Eq. (3.7), the projection is made on only the first term (3.1), so that neither $\varphi_n^{(N)}(n>0)$ nor $\varphi_0^{(\mathrm{pol})}$ appears quadratically in any of the equations. To repeat the particular cogency of this procedure: the exchange symmetry of the total wave function (3.6) being known, one in fact has some information about short-range correlations which will be retained in the complete problem providing the integral in (3.7) is carried out with no further approximations. Clearly the validity of this argument also extends to the inclusion of the first-order permanent distortion moment $\varphi_2^{(2)}$ as well as the inclusion of $\varphi_0^{(\mathrm{pol})}$.

The carrying out of the integrations in (3.7) to obtain the explicit form of the radial equations for the u_{lm} is, aside from the Sloan[14] terms, a straightforward albeit tedious affair. Use is made in several places of the equations which the various radial functions satisfy. Since we confine our calculations to s- and p-wave scattering (beyond that, the various partial waves will become coupled), we shall give the equations for each partial wave separately in order to avoid the implication that they hold uncoupled for arbitrary l.

S wave:

$$\left[\frac{d^2}{dr^2}+V_0-2\int_0^\infty g_0(r,x)[\varphi_0^N(x)]^2dx+k^2\right]u_{00}(r)\pm\varphi_0^{(N)}(r)\int_0^\infty\varphi_0^{(N)}(x)[k^2-E_N+2/R_{AB}-2g_0(r,x)]u_{00}(x)\,dx$$
$$\mp\frac{\delta_{N2}}{\sqrt5}\varphi_0^{(2)}(r)\int_0^\infty\varphi_2^{(2)}(x)V_2(x)u_{00}(x)\,dx=-\frac{u_{00}(r)}{r^4}\,\tfrac{2}{3}\int_0^r\varphi_0^{(N)}(x)\,x\varphi_0^{(\mathrm{pol})}(x)\,dx\mp r\varphi^{(\mathrm{pol})}(r)\,\tfrac{2}{3}\int_r^\infty\frac{\varphi_0^{(N)}(x)u_{00}(x)\,dx}{x^4}. \qquad (3.8a)$$

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[12] A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) **A240,** 284 (1957).

[13] A. Temkin and J. C. Lamkin, Phys. Rev. **121,** 788 (1961).

[14] I. H. Sloan, Proc. Roy. Soc. (London) **A281,** 151 (1964).

P wave:

$$\begin{aligned}&\left[\frac{d^2}{dr^2}-\frac{2}{r^2}-2\int_0^\infty g_0[\varphi_0^{(N)}]^2dx+V_0-\tfrac{1}{5}(3m^2-2)V_2+\frac{2\delta_{N2}}{\sqrt{5}}\tfrac{1}{5}(3m^2-2)\int_0^\infty g_2\varphi_0^{(2)}\varphi_2^{(2)}dx+k^2\right]u_{1m}(x)\\
&\quad\mp\tfrac{2}{3}\varphi_0^{(N)}\int_0^\infty g_1\varphi_0^{(N)}u_{1m}dx\pm\tfrac{2}{3}\left(\frac{3m^2-2}{\sqrt{5}}\right)\delta_{N2}\varphi_2^{(2)}\int_0^\infty\varphi_0^{(2)}g_1u_{1m}dx=-\tfrac{2}{3}\frac{u_{1m}(r)}{r^4}\int_0^r\varphi_0^{(N)}x\varphi_0^{(\mathrm{pol})}dx\\
&\quad\mp\{\tfrac{1}{3}\varphi_0^{(\mathrm{pol})}[(E_N-k^2-2/R_{AB})+\tfrac{1}{5}(3m^2-2)V_2]+\tfrac{2}{3}r\varphi_0^{(0)}\}\int_r^\infty dx\frac{\varphi_0^{(N)}u_{1m}}{x^2}\mp\tfrac{1}{3}\left(\frac{3m^2-2}{5}\right)\varphi_0^{(\mathrm{pol})}\int_r^\infty dx\frac{\varphi_0^{(N)}V_2u_{1m}}{x^2}\\
&\quad\mp\tfrac{2}{3}\varphi_0^{(\mathrm{pol})}\int_r^\infty dx\varphi_0^{(N)}[g_0+\tfrac{2}{5}g_2]\frac{u_{1m}}{x^2}\mp\left\{\tfrac{2}{3}\frac{\varphi_0^{(N)}u_{1m}}{r^2}\left[\frac{d}{dr}\varphi_0^{(\mathrm{pol})}(r)\right]+\tfrac{1}{3}\varphi_0^{(\mathrm{pol})}\frac{d}{dr}\left[\frac{\varphi_0^{(N)}(r)u_{1m}(r)}{r^2}\right]\right\}.\qquad(3.8\mathrm{b})\end{aligned}$$

The terms on the right-hand side of these equations are the polarization terms; they therefore correspond to the ansatz (3.6b) for the complete wave function. In the no-polarization approximations, corresponding to (3.6a), the right-hand side of Eqs. (3.8) are to be set equal to zero. Note that in the first curly bracket on the right-hand side of (3.8b) the function is $\varphi_0^{(0)}$ independent of the order approximation N for the target wave function. This comes about because we assume $\varphi_0^{(\mathrm{pol})}$ satisfies (3.2) in all cases. The final curly bracket in (3.8b) contains the Sloan terms[14] which arise when proper account is take of the step function in (3.6b)[15] [cf. the discussion after Eq. (3.5)].

Since we compare the u_{lm} with unperturbed *Coulomb* waves of unit charge

$$\lim_{r\to\infty}F_l(r)=\sin[kr+(1/k)\ln 2kr-\tfrac{1}{2}\pi l+\sigma_l],\qquad(3.9)$$

to find the residual phase shift η_{lm}, it is essential from Eqs. (3.8) the $\varphi_0^{(N)}$ be normalized to unity. This is automatically the case in zeroth order ($\varphi_0^{(0)}$), but in first order this has necessitated a slight renormalization of the functions given in Table I. Accordingly we utilize functions $\bar{\varphi}_n^{(2)}$,

$$\bar{\varphi}_n^{(2)}(r)=1.017\varphi_n^{(2)}(r),\qquad n=0,2\qquad(3.10)$$

in place of $\varphi_n^{(2)}$ in the radial Eqs. (3.8) corresponding to the first-order approximations. Finally we mention again[13] that the formally divergent integrals in (3.8) give rise to well defined terms in the radial equations. For calculational convenience they have been regularized by the inclusion of a parameter Δ in the denominators of those terms and selected runs were tested to make sure that the phase shifts were satisfactorily independent of Δ.

IV. RESULTS AND DISCUSSION

The s-wave shifts are given in Table II and p-wave phase shifts are given in Table III (singlet) and Table IV (triplet). The dominant modification of the s-wave zeroth-order exchange approximate results comes from the induced polarization effects rather than the first-order permanent distortion moment. We believe that this dominance will be qualitatively true of scattering from most diatomic molecules of not too small polarizability and not too large internuclear separation.

The p-wave results are perhaps the most interesting and most unexpected. They are given in Tables III and IV. It can be seen from Table IV that the $m\equiv0$ triplet phase shifts are considerably larger than the s-wave phase shifts; their magnitude can be attributed to two causes which are not present for s waves. First we note from (3.8b) that the p-wave equations contain a quadrupole term, $V_2(r)$, which goes like r^{-3} for r large[16] and arises directly as a result of the elongation in the z direction of H_2^+. Aside from the Coulomb interaction itself, this is the longest range potential, and in the $m=0$ case it is attractive and accounts for about half of the calculated magnitude. The remainder arises from a rather subtle exchange effect. Because the orbital electron in H_2^+ is at a much larger distance from the origin than its atomic counterpart[14] (the electron in He^+) it can, in the appropriate spin state, resonate very strongly with the incoming p-wave electron (which can be associated with a nonzero impact parameter) to cause a large probability of exchange. It will be of considerable interest to see if an analogous situation could cause the feature which has been interpreted as a broad resonance[17] in low-energy $e-\mathrm{H}_2$ scattering. Equation (3.8b) also shows that there are also quadrupole potentials which can arise only in first order. Again because of the dominant effect of exchange

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[15] The p-wave phase shifts given by the method of polarized orbitals for $e-\mathrm{H}$ scattering should therefore be amended from those of Ref. 13 to those calculated by Sloan, Ref. 14. As such they agree remarkably well with more accurately, *subsequently calculated* lower-bound p-wave phase shifts. Cf., for example, M. Gailitis, in *Abstracts of Papers of the 4th International Conference on the Physics of Electronic and Atomic Collisions* (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 10.

[16] Such a potential can alter the form of effective range expansions. Cf., B. R. Levy and J. B. Keller, J. Math. Phys. **4**, 54 (1962); T. F. O'Malley, Phys. Rev. **134**, A1188 (1964); H. B. Snodgrass, *ibid.*, **148**, 5 (1966); A. Dalgarno and N. F. Lane in the abstracts cited in Ref. 15, p. 49; N. F. Lane, *ibid.*, p. 214.

[17] G. J. Schulz and R. K. Asundi, Phys. Rev. Letters **15**, 946 (1965); Phys. Rev. **158**, 25 (1967).

Table II. S-wave phase shifts (in radians).

k^2 (Ry)	Singlet				Triplet			
	zeroth	first	zeroth + pol.	first + pol.	zeroth	first	zeroth + pol.	first + pol.
0.01	−0.601	−0.597	−0.429	−0.430	−0.012	+0.021	+0.062	+0.117
0.1	−0.610	−0.609	−0.439	−0.440	−0.034	0.000	0.040	0.094
0.2	−0.618	−0.618	−0.446	−0.449	−0.055	−0.023	0.018	0.071
0.3	−0.623	−0.625	−0.452	−0.456	−0.076	−0.045	−0.003	0.049
0.4	−0.627	−0.629	−0.455	−0.461	−0.095	−0.065	−0.022	0.028
0.5	−0.628	−0.632	−0.458	−0.464	−0.112	−0.084	−0.039	0.009
0.6	−0.629	−0.634	−0.460	−0.467	−0.128	−0.101	−0.056	−0.009
0.7	−0.629	−0.635	−0.460	−0.469	−0.144	−0.118	−0.071	−0.076
0.8	−0.628	−0.635	−0.461	−0.470	−0.158	−0.133	−0.085	−0.041
0.9	−0.626	−0.635	−0.461	−0.471	−0.171	−0.148	−0.098	−0.056
1.0	−0.624	−0.632	−0.461	−0.471	−0.184	−0.161	−0.110	−0.070
2.0	−0.595	−0.609	−0.451	−0.464	−0.273	−0.262	−0.200	−0.176
3.0	−0.567	−0.581	−0.441	−0.453	−0.323	−0.321	−0.253	−0.243
4.0	−0.543	−0.557	−0.431	−0.442	−0.352	−0.355	−0.286	−0.286
5.0	−0.522	−0.537	−0.422	−0.432	−0.368	−0.374	−0.307	−0.315

Table III. Singlet P-wave phase shifts (in radians).

k^2 (Ry)	$m=0$				$\|m\|=1$			
	zeroth	first	zeroth + pol.	first + pol.	zeroth	first	zeroth + pol.	first + pol.
0.01	0.447	0.318	0.586	0.493	−0.474	−0.433	−0.326	−0.308
0.1	0.450	0.325	0.584	0.489	−0.469	−0.430	−0.321	−0.304
0.2	0.456	0.335	0.585	0.489	−0.464	−0.426	−0.314	−0.298
0.3	0.462	0.345	0.585	0.492	−0.457	−0.422	−0.306	−0.292
0.4	0.467	0.354	0.586	0.495	−0.450	−0.417	−0.297	−0.286
0.5	0.470	0.363	0.586	0.498	−0.443	−0.412	−0.288	−0.279
0.6	0.473	0.370	0.586	0.501	−0.435	−0.406	−0.279	−0.272
0.7	0.474	0.375	0.584	0.503	−0.427	−0.400	−0.269	−0.264
0.8	0.474	0.380	0.582	0.504	−0.420	−0.394	−0.261	−0.257
0.9	0.474	0.384	0.579	0.504	−0.412	−0.388	−0.252	−0.250
1.0	0.472	0.386	0.576	0.504	−0.404	−0.382	−0.244	−0.243
2.0	0.433	0.375	0.522	0.475	−0.340	−0.330	−0.183	−0.191
3.0	0.378	0.335	0.458	0.425	−0.301	−0.297	−0.155	−0.165
4.0	0.323	0.288	0.398	0.373	−0.278	−0.277	−0.144	−0.154
5.0	0.273	0.243	0.343	0.323	−0.264	−0.264	−0.141	−0.150

Table IV. Triplet P-wave phase shifts (in radians).

k^2 (Ry)	$m=0$				$\|m\|=1$			
	zeroth	first	zeroth + pol.	first + pol.	zeroth	first	zeroth + pol.	first + pol.
0.01	1.202	1.210	1.329	1.377	0.153	0.114	0.265	0.220
0.1	1.143	1.150	1.263	1.308	0.144	0.109	0.244	0.224
0.2	1.089	1.095	1.203	1.246	0.133	0.101	0.222	0.186
0.3	1.043	1.048	1.152	1.193	0.121	0.093	0.202	0.169
0.4	1.003	1.007	1.108	1.146	0.110	0.083	0.183	0.154
0.5	0.967	0.970	1.069	1.105	0.098	0.074	0.166	0.139
0.6	0.934	0.937	1.033	1.067	0.087	0.065	0.150	0.125
0.7	0.905	0.907	1.002	1.033	0.077	0.056	0.135	0.112
0.8	0.878	0.879	0.972	1.002	0.066	0.048	0.122	0.100
0.9	0.853	0.854	0.944	0.974	0.057	0.039	0.109	0.089
1.0	0.830	0.830	0.919	0.947	0.048	0.031	0.097	0.078
2.0	0.655	0.651	0.730	0.748	−0.023	−0.032	+0.010	−0.003
3.0	0.537	0.530	0.602	0.615	−0.068	−0.075	−0.042	−0.052
4.0	0.446	0.438	0.506	0.515	−0.099	−0.104	−0.077	−0.086
5.0	0.373	0.364	0.427	0.434	−0.121	−0.126	−0.101	−0.109

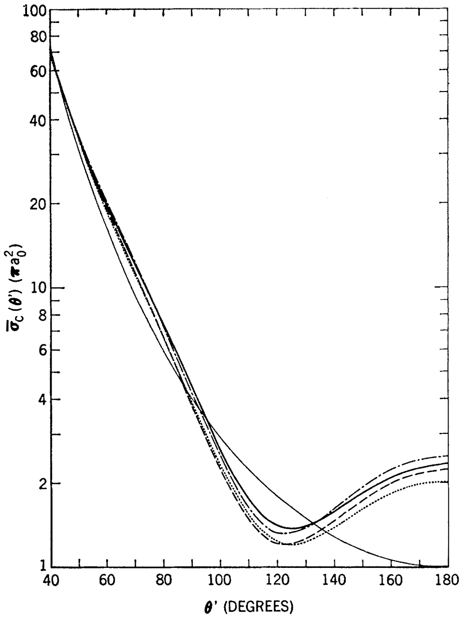

FIG. 1. Angular distribution $k^2=0.5$ (6.8 eV) in the following approximations: first+polarization (heavy solid), zeroth+polarization (dot-dash), first (dot), zeroth (dash), pure Coulomb (light solid).

in the triplet case, the large effect of the first-order terms compared to the polarization effects (relative to the s-wave results) only show up clearly in the singlet phase shifts (Table III).

Figures 1 and 2 give some angular distributions. They are designed to show the effects of the various approximations and spin states compared to each other as well as compared to pure Coulomb scattering. Qualitatively all approximations are of course indistinguishable from pure Coulomb scattering in the forward directions, dip below it at around 100°, and are substantially larger in the backward directions. In view of the size of the p-wave shifts, it will be necessary to include at least d waves in order to be sure that the qualitative features are not altered. In the d wave we encounter the first problem of coupling to different partial waves (the s wave in this case), so that such a calculation is sufficiently complex to be deferred to a later time.

One could also in the context of the present method readily include higher electronic states. In the zeroth-order–no-polarization approximation this would be an exact counterpart of the close-coupling expansions for electron-hydrogen scattering.[18] In addition to providing an alternate description of polarization, such states will allow for a direct calculation of inelastic scattering. Very likely they will also yield the molecular (electronic) counterpart of the resonances that have been calculated in electron-atom scattering.

Our aim in this investigation has been to develop the essential ideas for calculating the electronic part of low-energy electron-diatomic molecule generally. The next step in such applications is clearly $e-H_2$ scattering. It may seem that carrying through this calculation will be very straightforward, since the single-center (partial wave) theory for H_2 has been developed[19] and calculations including the ground Σ_g^+ performed.[20] However, these wave functions are in terms of the coordinates r_1, r_2, r_{12}; thus they pose nontrivial integration problems. Nevertheless we[21] can report that these integrations problems have been overcome, so that phase shifts corresponding at least to the zeroth-order–no-polarization approximation should be calculable in the not too far distant future. Carter, March, and Vincent[22] have in effect attempted to calculate in a similar approximation to this one using a single-center form of the H_2 wave depending only on r_1 and r_2. Also they have only estimated the effects of exchange, nevertheless the qualitative agreement of their results with Massey and Ridley[2] gives some confidence that when the present approach is accurately carried through, it will give very satisfactory phase shifts.

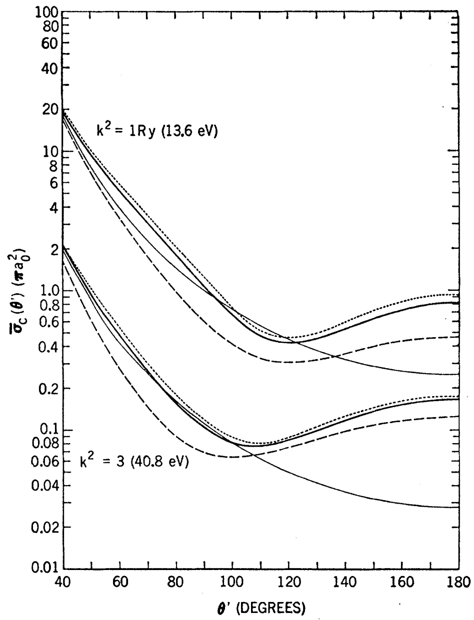

FIG. 2. Angular distributions in different spin states in first+polarization approximation for energies given: singlet (dash), triplet (dot), average (heavy solid), pure Coulomb (light solid).

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[18] Cf., P. G. Burke and K. Smith, Rev. Mod. Phys. **34**, 458 (1962).

[19] A. Temkin and A. K. Bhatia, J. Chem. Phys. **42**, 644 (1965).

[20] A. K. Bhatia and A. Temkin, J. Chem. Phys. **44**, 3656 (1966).

[21] The work in question is being carried out by one of us (A.T.) in collaboration with A. K. Bhatia.

[22] C. Carter, N. March, and D. Vincent, Proc. Phys. Soc. (London) **71**, 2 (1958).

For many electron-diatomic molecules it is clear that a single-center Slater determinant provides the practical counterpart of the zeroth-order wave function. This also allows polarization to be handled in analogy with electron-atom scattering.[9,23] This approximation will also automatically yield at least part of the quadrupole potential.

With regard to the further applicability of single-center wave functions to collision problems, Khare[24] has found that single-center wave functions yield surprisingly good results for excitation of H_2 by electron impact when used within the confines of the Born-Ochkur approximation. More recently[25] he has extended his calculations to the photoionization of H_2 using final-state wave functions of the present method suitably modified to the equilibrium separation $R_{AB}=1.4$ of H_2. His results thus far are very encouraging.

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Theory of High-Energy Inelastic Collisions between Molecular Systems. Dissociation of H_2^+ on Collision with H_2†

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Inelastic collisions between the hydrogen molecule ion (H_2^+) and the hydrogen molecule are investigated theoretically within the framework of the first Born approximation. The possibility that H_2^+ may be in an excited vibrational state before the collision takes place is given special consideration. Appropriate sums of the theoretical cross sections are identified with the experimental measurements of the cross section σ_1, for the dissociation of H_2^+ into a proton and hydrogen atom, and of $\sigma_1+\sigma_2$, where σ_2 is the ionization cross section of H_2^+. Agreement is good between theory and σ_1 for collision energies greater than 50 keV and between theory and $\sigma_1+\sigma_2$ for collision energies greater than 1 MeV. Any discrepancies between experiment and theory can be identified as either the expected failure of the Born approximation at low energies or the omission of certain inelastic processes in the theoretical results.

I. INTRODUCTION

A SERIES of recent papers[1–4] has treated the electronic excitation of the hydrogen molecule ion (H_2^+) when scattered by a structureless charged particle. One of these publications[3] also included a treatment of H_2^+ collisions with hydrogen atoms and a recommendation that the approach developed in this paper could be used for complicated neutral targets. A study of this nature for the $H_2^+-H_2$ scattering system is the object of the present paper.

The collision of interest is

$$H_2^+(0)+H_2(0)=H_2^+(n)+H_2(N). \qquad (1)$$

The electronic states are indicated in parentheses; the zeros stand for the ground electronic states and it is stipulated that $n\neq 0$ but N may be equal to 0. If it is assumed that (1) all n lead to the dissociation of H_2^+ and (2) no other mechanism, such as direct vibrational dissociation, contributes in an important way to dissociation, the experimental results on H_2^+ dissociation can be identified with the theoretical data provided here. Experimental studies detect fast protons and/or hydrogen atoms from the dissociation of H_2^+ and the final state of the target is usually not specified. The cross section for proton–plus–hydrogen-atom production is designated σ_1 and the total proton production is called $\sigma_1+2\sigma_2$, where σ_2 is the cross section for

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* 1965 Summer employee of Sandia Laboratory.

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